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Ferroelectric and Piezoelectric Properties of Odd-Numbered Nylons

by

J.I. Scheinbeim, B.A. Newman, B. Zhang-Mei and J.W. Lee

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**FERROELECTRIC AND PIEZOELECTRIC PROPERTIES
OF ODD-NUMBERED NYLONS**

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ABSTRACT

J.I. Scheinbeim, B.A. Newman, B. Zhang-Mei and J.W. Lee
Polymer Electroprocessing Laboratory
Rutgers University

"High Temperature Stable Piezoelectric Polymers: the Odd-Numbered Nylons"

Recent discoveries in our laboratory of a new class of ferroelectric polymers--the odd numbered nylons--led to another important discovery: a mechanism for the stabilization of the remanent polarization in these materials to their crystalline melting point. As the piezoelectric response of ferroelectric polymers is as stable as their remanent polarization, we have produced a set of high temperature stable piezoelectric polymers which can easily operate in a temperature range up to $\sim 250^{\circ}\text{C}$.

In addition, we have now begun to examine new types of piezoelectric polymer films consisting of co-electroprocessed layers of odd numbered nylon film and poly(vinylidene fluoride) PVF_2 film, which are shown to exhibit a significantly enhanced response, compared to that of either component. Enhanced response is also observed for blended powders of PVF_2 and a copolymer of vinylidene fluoride and tri-fluoroethylene.

Recent studies in our laboratory (The Polymer Electroprocessing Laboratory, Rutgers University) have led to the discovery of a new class of ferroelectric polymers--the odd numbered nylons (1,2). The ferroelectric switching behavior of these nylons can be seen in Figures 1 and 2, which show the current density (J) versus electric field (E), and electric displacement D versus electric field (E) behavior, respectively, of Nylon 11, Nylon 9, Nylon 7 and Nylon 5. Figure 3 shows the remanent polarization as a function of dipole density for these nylons. The remanent polarization appears to linearly increase from a value of $\sim 55 \text{ mC/m}^2$ for Nylon 11 to a value of $\sim 135 \text{ mC/m}^2$ for Nylon 5. If we project this linear increase to the dipole density of Nylon 3, we obtain a value $\sim 180 \text{ mC/m}^2$. The actual value for Nylon 3 will hopefully be determined in the near future and will be compared with the projected value.

In addition, we have also discovered an electroprocessing technique for stabilizing the polarization of these materials to about their crystalline melting points, which has resulted in a new class of piezoelectric polymers that can be used at high temperatures (3). We have extended our previous work on Nylon 11 and Nylon 7 to include studies of Nylon 9 and Nylon 5. Nylon 5, which has the highest melting point of any of the odd-numbered nylons we have studied, has now been shown to exhibit stable piezoelectric response up to a use temperature of $\sim 250^\circ\text{C}$.

The temperature dependence of the piezoelectric strain constants, d_{31} , for

the odd-numbered nylons studied are shown in Figure 4, and the temperature dependence of the corresponding piezoelectric stress constants are shown in Figure 5.

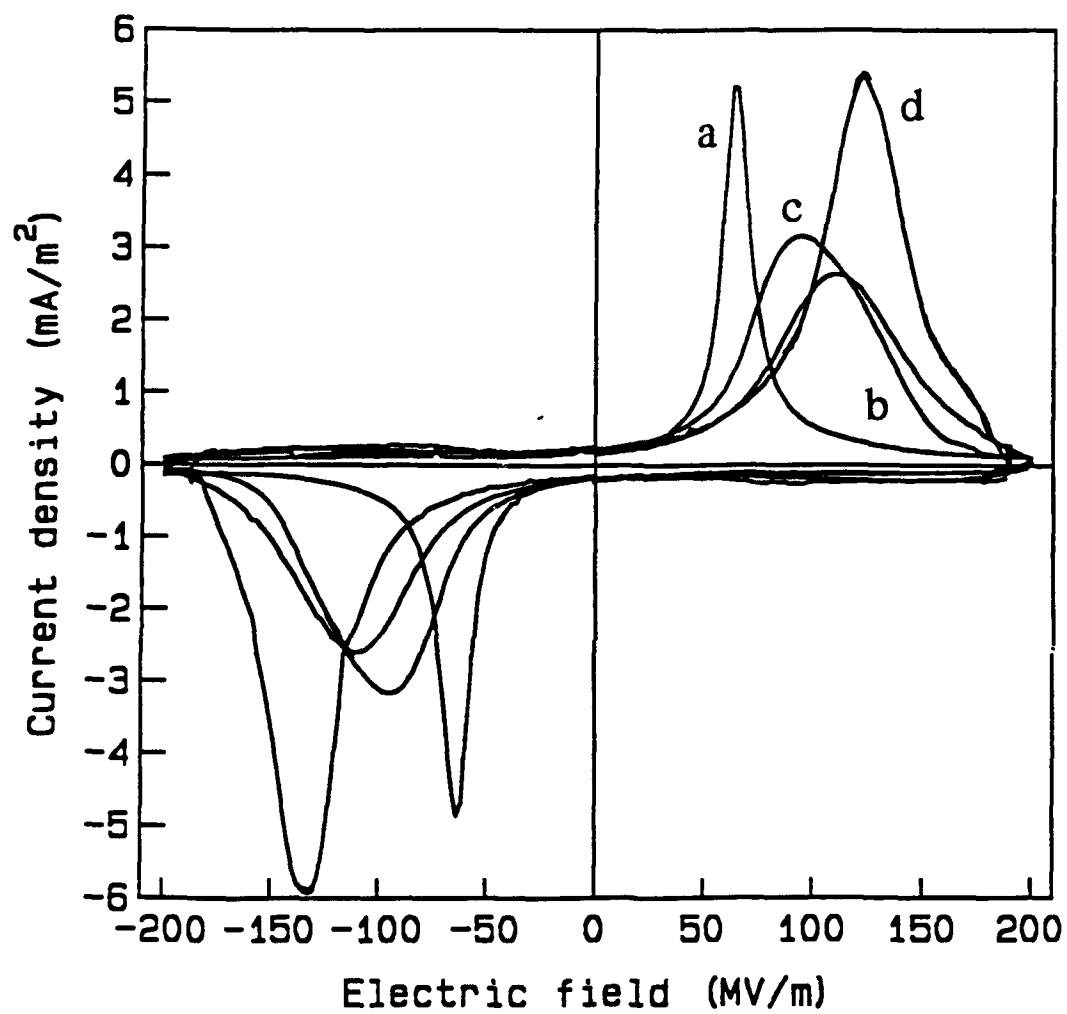
In all cases, the piezoelectric response of these odd numbered nylons is low at room temperature, which is below their glass transition temperature, T_g . As temperature increases through T_g , piezoelectric response exhibits a sigmoidal shaped increase followed by a plateau region, and sometimes a decrease in response as the maximum annealing temperature of each sample is reached. Each of the polarized nylon samples was first annealed for two hours at the highest measurement temperature shown, in order to stabilize their response.

Acknowledgements

This work was supported by DARPA and the Office of Naval Research.

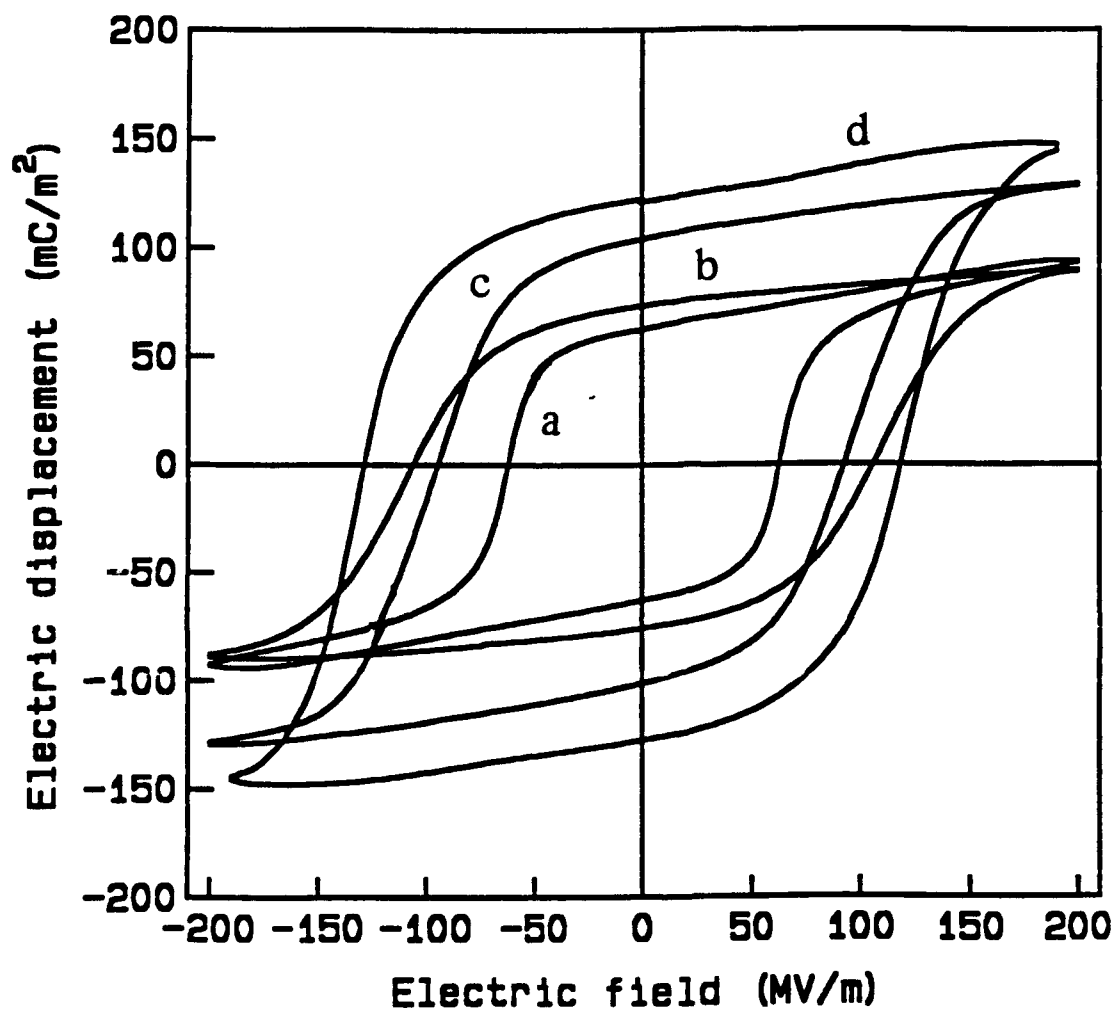
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3. "High-Temperature Characteristics of Nylon-11 and Nylon-7 Piezoelectrics," Y. Takase, J.W. Lee, J.I. Scheinbeim, and B.A. Newman, Macromolecules, 24, 6644-6652 (1991).



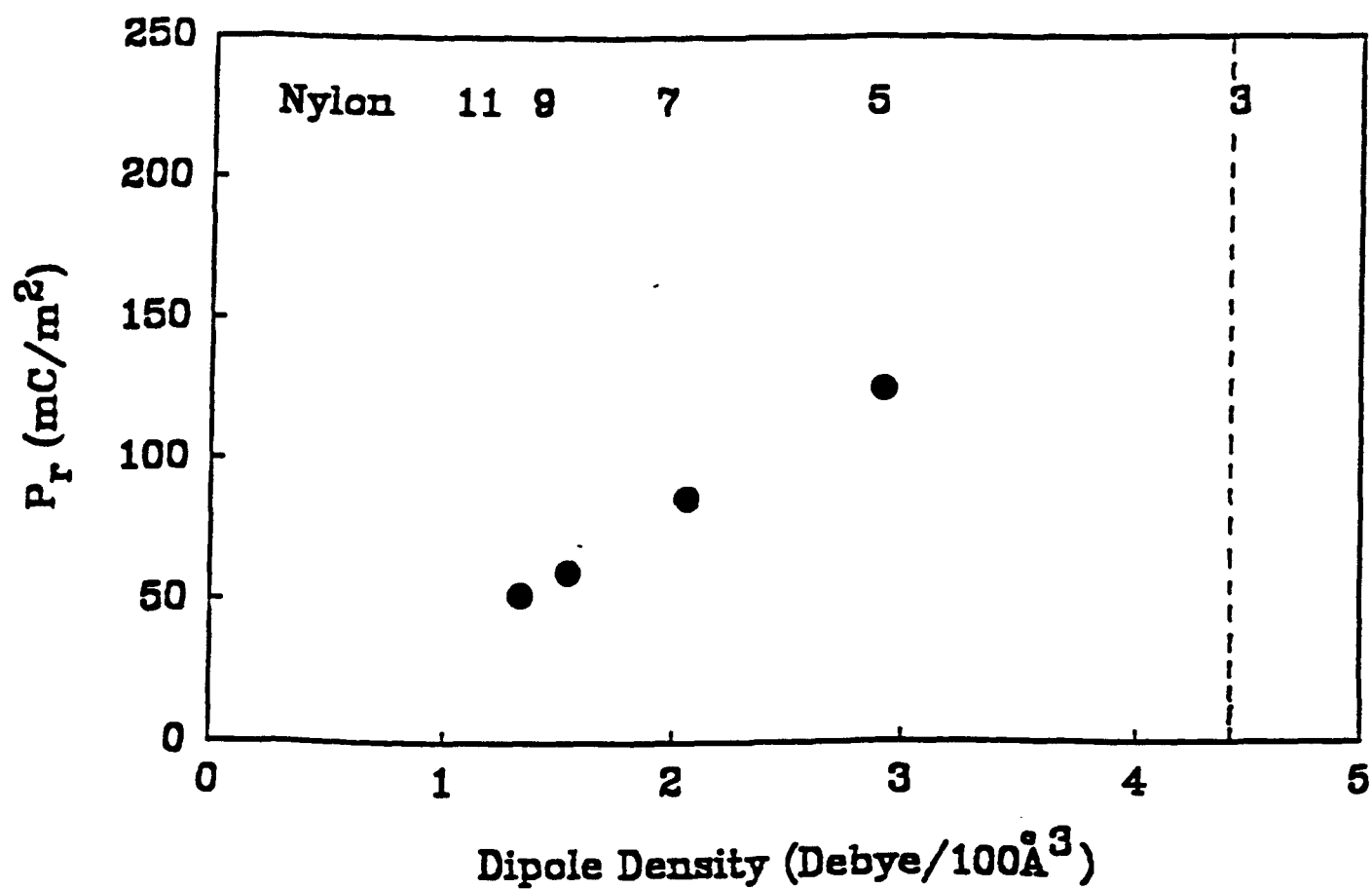
**Current density versus electric field for
a) Nylon 11, b) Nylon 9, c) Nylon 7, and
d) Nylon 5**

Figure 1



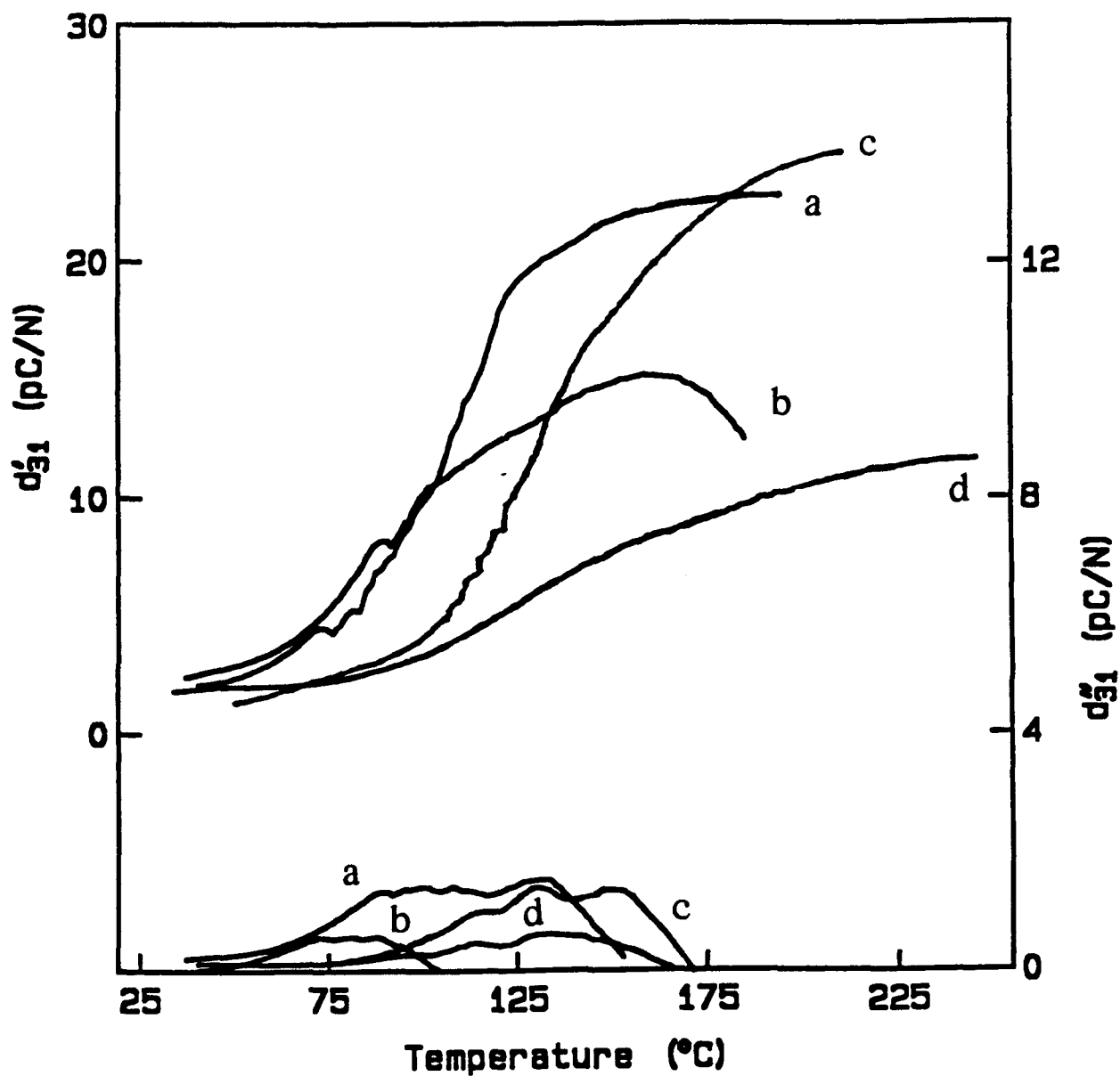
D - E hysteresis loops of odd Nylons. a) Nylon 11, b) Nylon 9, c) Nylon 7 and d) Nylon 5

Figure 2



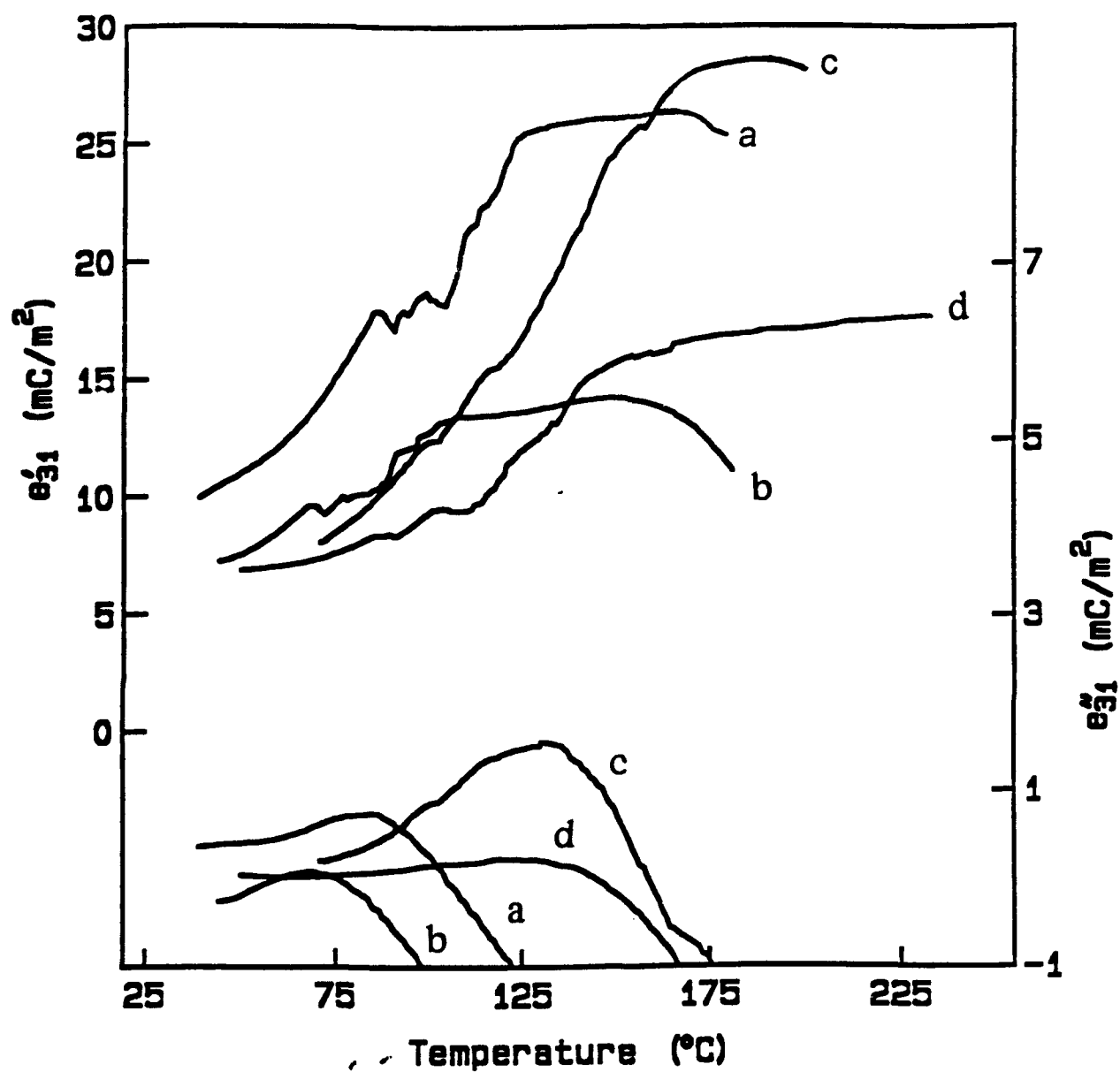
Dependence of remenant polarization on the
dipole density of odd Nylons

Figure 3



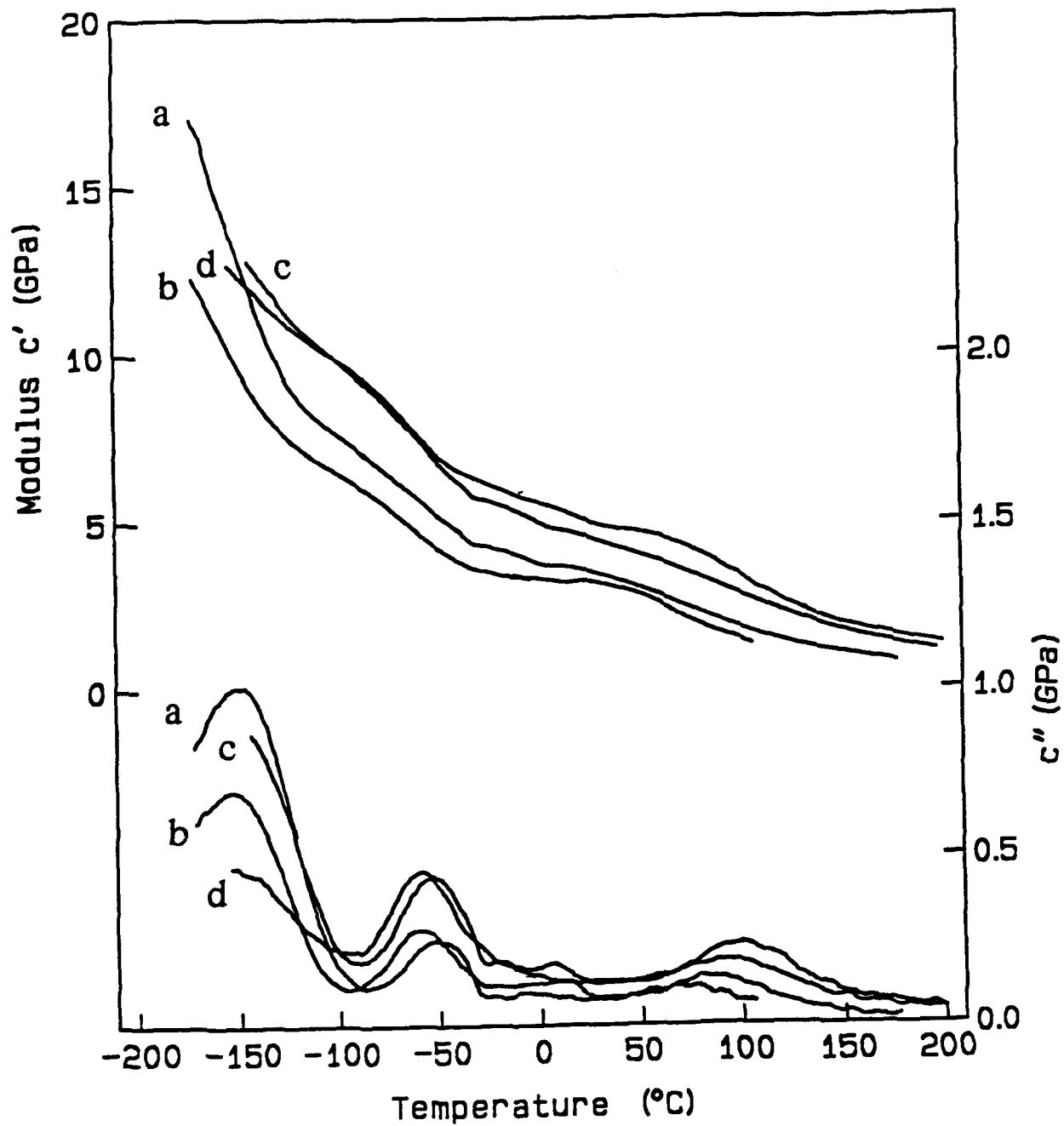
Temperature dependence of the piezoelectric strain constants, d_{31} , of samples of a) Nylon 11, b) Nylon 9, c) Nylon 7 and d) Nylon 5 measured at 104 Hz

Figure 4



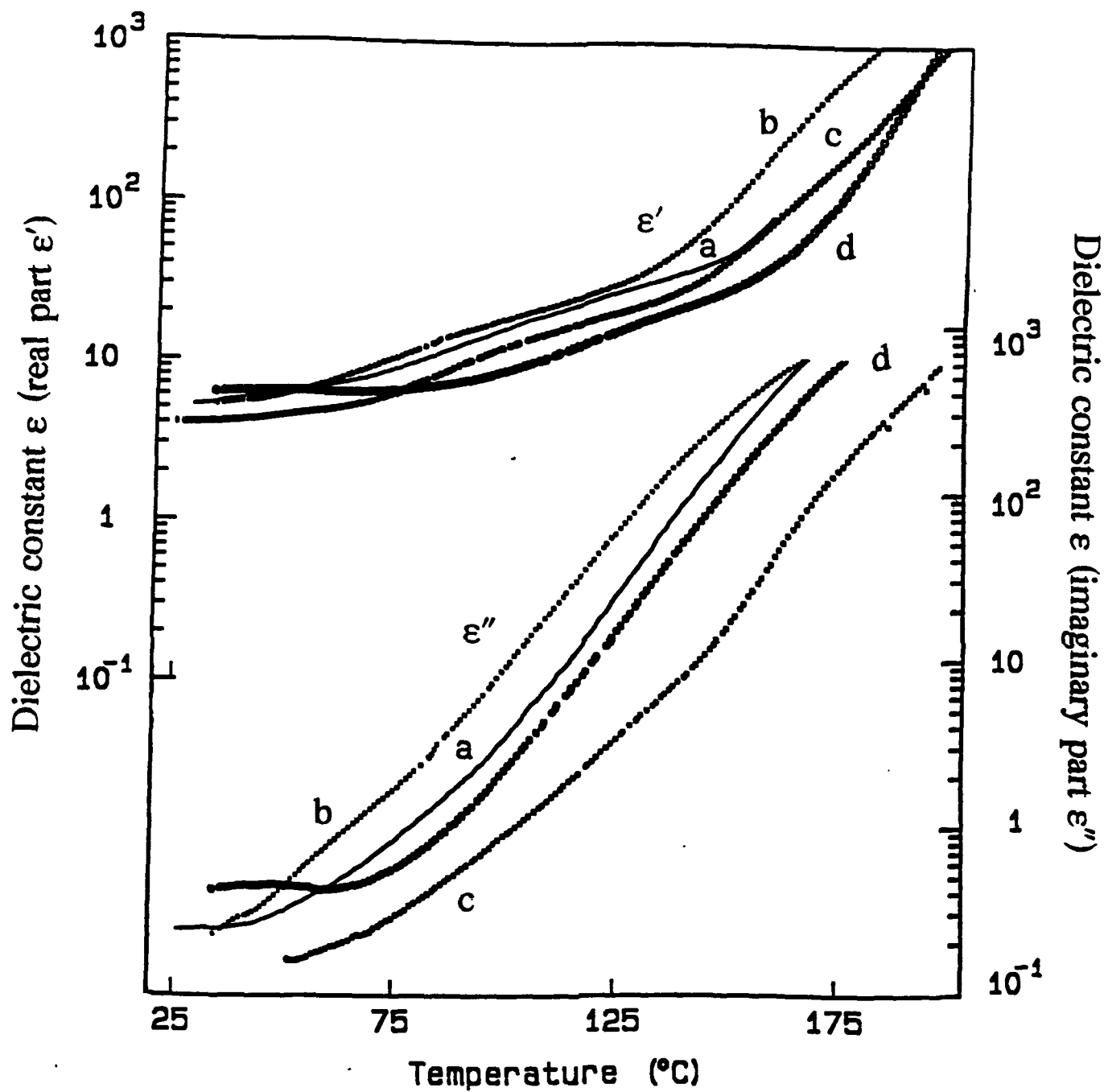
Temperature dependence of the piezoelectric stress constants, e_{31} , of samples of a) Nylon 11, b) Nylon 9, c) Nylon 7 and d) Nylon 5 measured at 104 Hz

Figure 5



Temperature dependence of the modulus (real part c' , and imaginary part c'') for samples of a) Nylon 11, b) Nylon 9, c) Nylon 7, and d) Nylon 5 measured at 104 Hz

Figure 6



Logarithmic plot of dielectric constants as a function of temperature for a) Nylon 11, b) Nylon 9, c) Nylon 7 and d) Nylon 5 measured at 104 Hz

Figure 7

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